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Photocatalysis of β-blockers – An overview

Marothu Vamsi Krishna [a,*], Gorrepati Madhavi [b], Nagi F. Idris [c], Salah Ali M. Idris [d], Lella Ravi Kiran Chowdary [e]

[a] Faculty of Pharmacy, Omar Al-Mukhtar University, Tobruk, Libya
[b] University College of Pharmaceutical Sciences, Acharya Nagarjuna University, Nagarjuna Nagar, India
[c] Faculty of Pharmacy, Omar Al-Mukhtar University, Al-Beida, Libya
[d] Department of Chemistry, Faculty of Science, Omar Al-Mukhtar University, Tobruk, Libya
[e] Alliance Institute of Advanced Pharmaceutical and Health Sciences, Hyderabad, India

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Abstract Photocatalysis is one of the most effective advanced oxidation processes to remove residual pharmaceuticals from the aquatic environment. β-Blockers are the group of pharmaceuticals commonly found in the environment and are showing potential risk to the aquatic and terrestrial organisms. This paper provides an overview of different photocatalytic procedures found in the literature for the abatement of β-blockers.

1. Introduction

Beta (β)-blockers are a class of drugs used to treat a variety of cardiovascular diseases, such as hypertension, coronary artery disease and cardiac arrhythmias, by blocking the action of adrenaline and noradrenaline on the β-adrenergic receptors in the body, primarily in the heart (Maurer et al., 2007). The most commonly used β-blockers are atenolol, propranolol and metoprolol, and the structures of those are shown in Fig. 1. Propranolol was the first clinically successful β-blocker developed (De la Cruz et al., 2013) and it has the highest acute and chronic toxicity within the class of β-blockers followed by metoprolol (Christensen et al., 2009; Fent et al., 2006; Maurer et al., 2007).

The presence of active pharmaceutical ingredients (APIs) in the aquatic environments was reported as early in the 1980s (Richardson and Bowron, 1985). It is an emerging environmental issue and provides a new challenge to drinking water, wastewater and water reuse treatment systems (Ikehata et al., 2006). The most important sources of pharmaceutical compounds in the environment are APIs administered to the patient's excreted either as metabolites or as the unchanged parent compounds, hospitals, pharmaceutical industry waste, and rejected drugs from households, waste water treatment plants and intensive animal breeding farms (Fatta et al., 2007). Pharmaceutical residues have been detected in many environmental matrices worldwide at concentrations ranging from ng/L to μg/L (Benner et al., 2009; Nicolaou et al., 2007; Santos et al., 2009; Ternes and Joss, 2006).This is of great concern in particular because of their potential impact on terrestrial and aquatic ecosystems and public health (Bendz et al., 2005; Cleuvers, 2005; Sharma, 2008).

* Corresponding author. Tel.: +218 944828805.
E-mail address: vkmarothu@gmail.com (V.K. Marothu).
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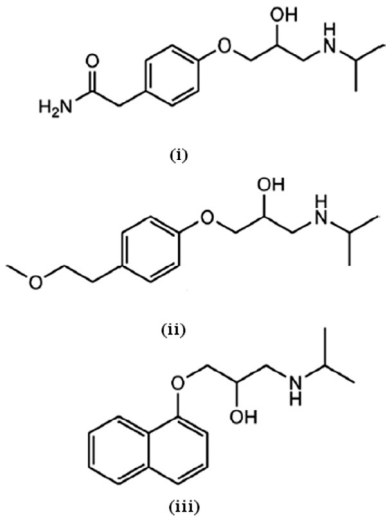


Figure 1 Chemical structures of (i) atenolol (ii) metoprolol (iii) propranolol.

The occurrence of β-blockers has been repeatedly reported in recent years in the effluents of many wastewater treatment plants around the world (Brun et al., 2006; Carlsson et al., 2009; Conkle et al., 2008; Gabet-Giraud et al., 2010; Huggett et al., 2003; Joakim Larsson and Fick, 2009; Liu and Williams, 2007; Nikolai et al., 2006; Sacher et al., 2001; Ternes, 1998). These compounds are persistent against biological degradation and natural attenuation, and therefore, may remain in the environment for a long time. Conventional wastewater treatment using activated sludge (Paxeus, 2004) is not effective in removing these compounds completely. The promising technology for the treatment of wastewaters containing pharmaceuticals is advanced oxidation processes (AOPs) (Dantas et al., 2011; Klavarioti et al., 2009). These techniques are based on the generation of hydroxyl radicals, which oxidize and mineralize all the organic compounds. Among AOPs, photocatalysis is an effective, low cost, environmental friendly and sustainable treatment technique. This process is based on the interaction of light and a semiconductor (catalyst). The most effective photocatalyst for this purpose is titanium dioxide (TiO_2) (Malato et al., 2002). A photon with energy higher than TiO_2 band gap (3.2 eV for anatase and 3.0 eV for rutile) arrives to the catalyst surface, an electron is photo excited from the valence to the conduction band; the wavelength range with energy higher than TiO_2 band gap is $\lambda < 390$ nm. This mechanism generates electron–hole pairs on the semiconductor surface which lead to a chain of redox reactions related to organic contaminants degradation (Fig. 2) (Chong et al., 2010). The photocatalytic oxidation of an organic species often proceeds via adsorption of the contaminant on the surface of the catalyst, followed by direct subtraction of the contaminant's electrons by positively charged holes. Another possible way is oxidation with OH radicals, generated from water of the aqueous environment, which takes place at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the contaminant. This review article provides an overview of different photocatalytic procedures found in the literature for the abatement of β-blockers in the aquatic environment.

2. Photocatalytic works on β-blockers

Yang et al. (2010) performed photocatalytic degradation kinetics of three β-blockers (atenolol, metoprolol and propranolol) in aqueous solution using Pyrex reactor. The light source used was high pressure mercury lamp and the photocatalyst was Degussa P25 (commercial TiO_2 powder). The three drugs were completely degraded within 40 min irradiation, using a TiO_2 concentration of 2.0 g/L. The degradation of the three drugs followed pseudo-first-order kinetics and degradation occurred mainly on the surface of TiO_2 by oxidation reactions with

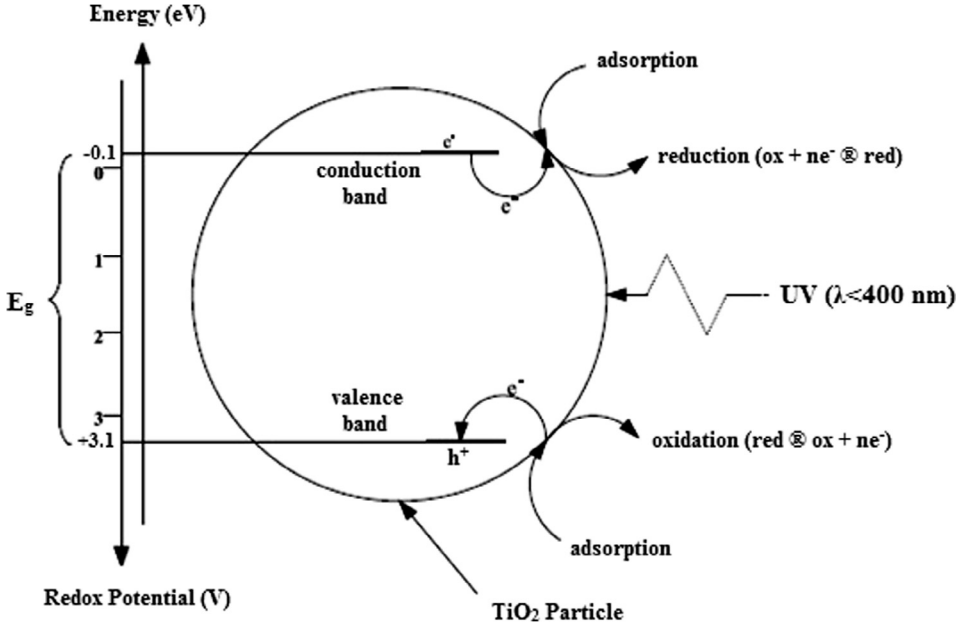
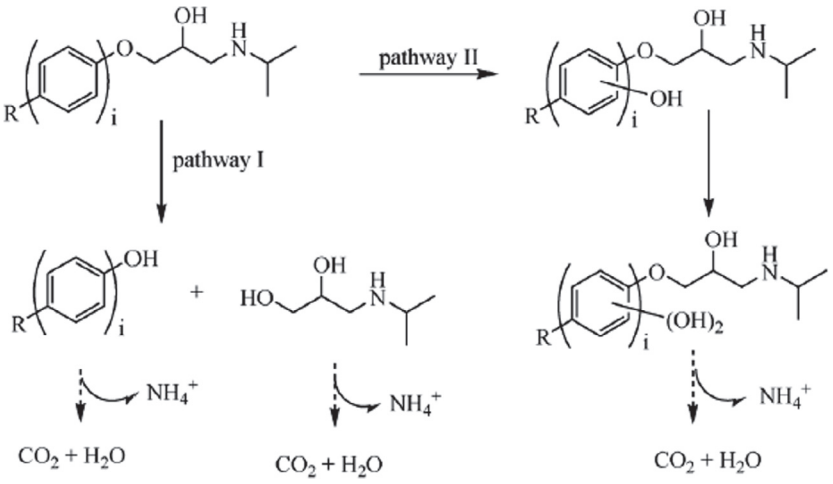


Figure 2 Principles of photocatalysis using TiO_2.



i = the number of aromatic rings, and R = the substituted group on aromatic ring. atenolol: i = 1, R = NH_2COCH_2-,; metoprolol: i = 1, R = CH_3OCH_2 CH_2-,; propranolol: i = 2, R = H.

Figure 3 General scheme of degradation pathways for β-blockers (Yang et al., 2010).

photohole (h^+) or OH radicals. Degradation intermediates were completely mineralized to CO_2 and nitrogen (predominantly as NH_3/NH_4^+) within 240 min. The major degradation pathways for the three β-blockers were cleavage of side chain (–CH (OH) CH_2 NH CH $(CH_3)_2$) and addition of –OH group to the parent compound. General scheme of degradation pathways for β-blockers is shown in Fig. 3 (Yang et al., 2010).

Ioannou et al. (2011) investigated decomposition of β-blockers (atenolol and propranolol) by means of TiO_2 photocatalysis using solar simulator in water and wastewater. Irradiation was provided by a 1 Kw Xe-OP lamp and photocatalyst used was Degussa P25. Different commercially available TiO_2 catalysts (Degussa P25, Hombicat UV100, Aldrich, Tronox AK-1, Tronox TRHP-2, Tronox TR) were used in the study and found that Degussa P25 is showing higher photocatalytic activity. This is due to its structure which is a mixture of anatase and rutile, and slower electron/hole recombination on the surface of Degussa P25. After 120 min of irradiation with Degussa P25 80% of the drug was decomposed. Degradation was favored in pure water compared with the wastewater because the latter contains dissolved organic carbon (DOC) and radical scavengers which show detrimental effect on conversions.

Toxicity of atenolol and propranolol before and after the photocatalytic treatment was evaluated by using *Daphnia magna*. Toxicity increased during the early stages of photocatalytic treatment for either substrate and then gradually decreased on prolonged treatment due to elimination of the substrate and its toxic reaction intermediates.

Ji et al. (2013) investigated photocatalytic degradation of atenolol in pH 6.8 Milli-Q water and river water using TiO_2 as catalyst. Efficiency of the four different TiO_2 catalysts (Hombicat UV100, Millennium PC500, Aldrich rutile and Degussa P25) was also investigated. Degussa P25 exhibited the highest photocatalytic activity. Complete degradation of atenolol was obtained after 60 min and 180 min of irradiation in pH 6.8 Milli-Q water and river water, respectively. Atenolol was degraded to 3-(isopropylamino)propane-1,2-diol, *p*-hydroxyphenylacetamide and 4-[2-hydroxy-3-(isopropylamino)propoxy] benzaldehyde through ether chain cleavage, hydroxylation and loss of $CONH_2$ from acetamide function group respectively. Hydroxy radical ($HO^{\cdot}$) was the predominant reactive species involved in the photocatalytic degradation of atenolol. Possible photocatalytic degradation pathways of atenolol are shown in Fig. 4. Intermediates formed during the photocatalysis further oxidized to five carboxylic acids namely oxalic, glyoxylic, malonic, oxamic and formic acid. In the river water atenolol degradation was slow due to the presence of inorganic ions and natural radical scavengers (Cl^-, CO_3^{2-}, HCO_3^- and dissolved organic matter). Inorganic ions compete for the active sites on the TiO_2 surface or they form salt layer on the TiO_2 surface and reducing/blocking the accessibility of catalyst and substrate (atenolol). Natural radical scavengers present in the river water reduce the $HO^{\cdot}$ concentration and thereby decreasing the photocatalytic efficiency.

Romero et al. (2011) investigated the degradation of metoprolol and propranolol by photocatalysis. Photocatalytic experiments were carried out with 0.4 g/L of TiO_2 as catalyst, 50 mg/L of both drugs and xenon lamp as irradiation source. Metoprolol and propranolol were completely removed after 300 and 360 min of irradiation, respectively. Biodegradability and toxicity tests were performed to assess the suitability of the photocatalytic treatment. Untreated samples were not biodegradable and treated samples were biodegradable through oxidation promoted by hydroxyl radicals. Biodegradability of the metoprolol was faster compared with the propranolol. Acute toxicity of both compounds prior and after the treatment was determined by measuring the inhibition of *Vibrio fischeri* bioluminescence. Toxicity of the metoprolol was reduced from the beginning of the treatment but for propranolol more toxic intermediates than the primary compound were formed in the early-stage of reaction, after 30 min of irradiation, the toxicity was decreased continuously.

De la cruz et al. (2013) assessed the propranolol degradation by direct photolysis and TiO_2 photocatalysis using solar and artificial (Xe-lamp) light. In this study photo-reactors made with quartz and Duran were tested and found that quartz reactor given significant propranolol degradation. In

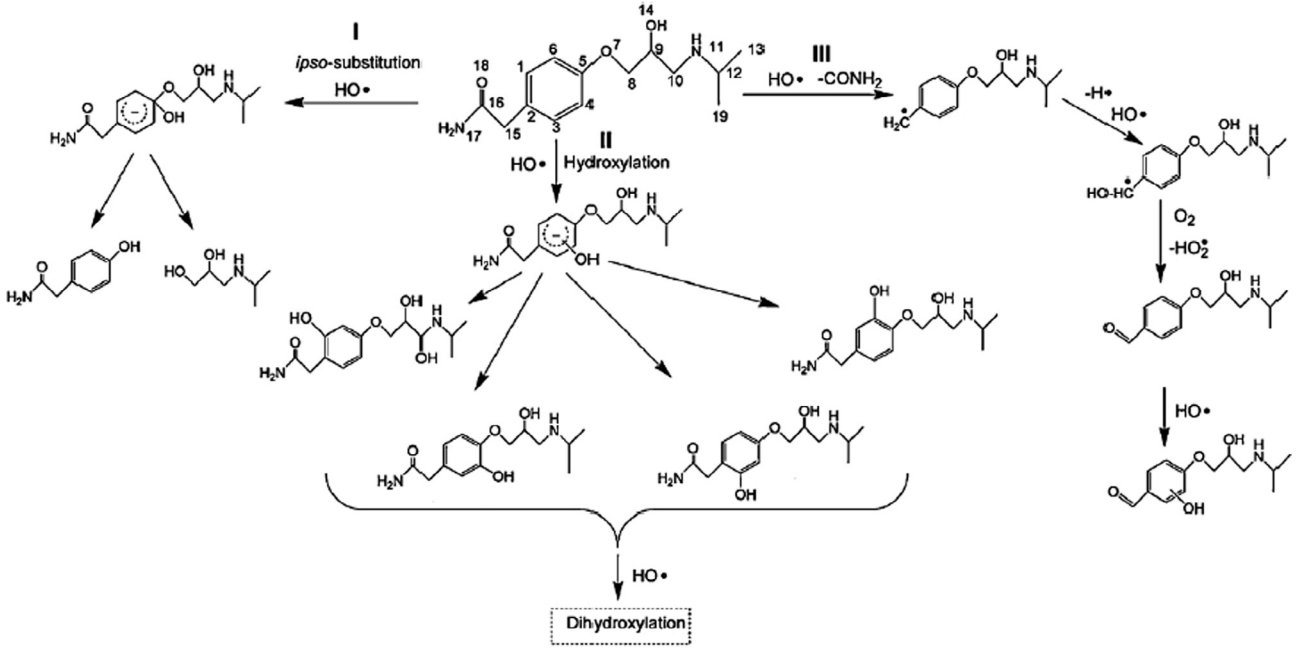


Figure 4 Photocatalytic degradation pathways for atenolol in aqueous TiO_2 suspensions (Ji et al., 2013).

the direct photolysis, after 240 min of irradiation 77% and 71% of the drug was degraded by the solar plant and the laboratory device (artificial light), respectively. Mineralization observed was 7% in the solar plant and 2% in the laboratory device.

In the photocatalysis treatment, concentration of TiO_2 used was 0.4 g/L and the degradation observed after 240 min of irradiation was 81% for the solar plant and 94% for lab device. Meanwhile mineralization reached was 30% and 41% in solar plant and laboratory device, respectively.

This study shown that photocatalysis is better than the photolysis in the propranolol degradation and mineralization. Mineralization was negligible in the photolysis compared with the photocatalysis because there are no other photosensitive compounds in water to generate hydroxyl radicals which are main reactive species for propranolol removal.

Rivas et al. (2010) investigated the efficiency of several UV-C radiation based methods for the mineralization of metoprolol. Mineralization was performed by means of UV-C, UV-C/H_2O_2, UV-C/percarbonate, UV-C/monopersulphate, UV-C/TiO_2, UV-C/H_2O_2/TiO_2 and photo-Fenton (Fe^{2+} and H_2O_2) reagent. Under UV-C radiation mineralization degree was negligible; addition of free radical promoters/photocatalysts significantly increases the degradation rate. Among the tested systems photo-Fenton reagent showed maximum efficiency (70% mineralization) due to three simultaneous actions in the process, direct photolysis, H_2O_2 photolysis and Fenton's reagent.

Czech and Rubinowska (2013) investigated the photocatalytic degradation of metoprolol in the tube reactor using four different commercially available TiO_2 samples (TiO_2-Tytanpol (T1), TiO_2-Sigma–Aldrich (T2), Hombikat-Sigma–Aldrich (T3) and TiO_2-S21-Sigma–Aldrich (T4)) differed in specific surface area, pore volume and rutile presence. Brunauer–Emmett–Teller (BET) surface areas (m^2/g) of T1, T2, T3 and T4 were 12.08, 11.50, 61.03 and 55.33, respectively. Metoprolol was most effectively removed by T3 and least effectively by T2. This study indicates that photocatalyst with highest BET surface area (T3) revealed the highest activity and lowest BET surface area (T2) revealed the lowest activity in metoprolol photocatalytic oxidation.

Ji et al. (2012) investigated the nitrate-induced photolysis behavior of atenolol and toxicity of its degradation products. Photolysis experiments were conducted under simulated solar irradiation using 1000 W Xe arc lamp. Influence of pH, bicarbonate concentration and dissolved organic matter (DOM) was also studied. Increase in the nitrate concentration increases the rate of reaction due to generation of hydroxyl radicals upon irradiation of nitrate solution.

Increase in pH decreases the reaction rate of atenolol by decreasing the rate of generation of hydroxyl radicals during irradiation of nitrate. Increase in bicarbonate concentration decreases the photodegradation rate of atenolol due to increase in pH and hydroxyl radical scavenging effect.

The presence of DOM decreases the photolysis rate constant; this is due to competition between DOM and nitrate ions for the photons. Less number of photons is available for exciting nitrate and thereby decreased the generation of hydroxyl radicals. During the photocatalysis process atenolol and its degradation products were monitored by HPLC and LC–MS. The major pathways of atenolol degradation were hydroxylation and side chain cleavage .The toxicity of the phototransformation products was evaluated by using *Daphnia magna* and the results revealed that they are less toxic. This study suggested that photodegradation was an important pathway for atenolol toxicity reduction in natural water containing relatively high concentration of nitrate.

Rey et al. (2012) prepared and characterized a TiO_2 magnetic activated carbon catalyst to mineralize metoprolol tartrate. The photocatalytic activity of the TiO_2 magnetic activated carbon catalyst was tested by performing degradation of metoprolol (Initial Concentration: 10 and 50 mg/L) under simulated solar photocatalytic ozonation. The results obtained were compared with those obtained from the

experiments of single adsorption (i.e., absence of radiation and ozone), single ozonation (i.e., absence of radiation and catalyst), catalytic ozonation (i.e., absence of radiation), photolytic ozonation (i.e., absence of catalyst), TiO_2 photocatalysis (i.e., absence of ozone) and photocatalytic ozonation with Degussa P25. Among the tested experimental conditions photocatalytic ozonation with Degussa P25 or TiO_2 magnetic activated carbon catalyst shown higher metoprolol removal rate and total organic carbon (TOC) degradation (mineralization) due to the production of large number of hydroxyl radicals. It was observed that efficiency of TiO_2 magnetic activated carbon catalyst was somewhat lower than that of the Degussa P25, even though, the prepared catalyst is an interesting alternative material for photocatalysis due to its stability and reusability. Photolytic ozonation was also equally effective that of photocatalytic ozonation when using a metoprolol initial concentration of 10 mg/L, this result provides a new way, solar photolytic ozonation for the degradation of emerging contaminants from water.

Abramovic et al. (2011) investigated the photocatalytic degradation of metoprolol tartrate in suspensions of two TiO_2-based photocatalysts (Degussa P25 or Wackherr) with different surface area. TiO_2 Wackherr has 6 times less surface area than Degussa P25. Faster degradation was observed with TiO_2 Wackherr compared to Degussa P25 due to lesser radiation scattering and slower back reactions, which compensate the lower surface area of TiO_2 Wackherr. In case of Degussa P25 slower initial degradation rate was observed due to higher radiation scattering and back reactions. After 240 min of irradiation metoprolol was mineralized completely in both the cases. Degradation intermediates were detected and identified by LC–DAD and LC–MS/MS techniques. Major degradation pathways involved in the photocatalysis of metoprolol are hydroxylation of the aromatic ring, shortening of the methoxyl-containing lateral chain and cleavage of, or addition of hydroxyl radical to, the amine-containing chain.

Santiago-Morales et al. (2013) studied visible light photocatalytic degradation of propranolol using cerium doped titanium dioxide as catalyst in ultrapure water and biologically treated wastewater. Cerium doping of TiO_2 increases the photocatalytic efficiency of TiO_2 by shifting its absorption from near UV region of the solar spectrum to the visible region. Photocatalysis of propranolol was carried out in a Duran tubular photoreactor with the concentration of 25 mg/L and radiation source is Xe-OP lamp with a photon flux of $(6.19 \pm 0.20) \times 10^{-6}$ Einstein/s (290–400 nm). Propranolol was completely disappeared in less than 2 h of irradiation. Photocatalytic rate was less in biologically treated wastewater compared with ultrapure water due to the presence of radical scavengers and competing substances. More than thirty reaction intermediates were formed during the process and those were detected by liquid chromatography coupled to quadrupole-time-of-flight mass spectrometry (LC-ESI-QTOF-MS/MS). The major degradation pathways of the propranolol are cleavage of the ether bond and addition of hydroxyl groups to the aromatic nuclei or to the ring opening attack of hydroxyl radicals on the naphthol moiety. The toxicity of the degradation products was determined using the green algae *Pseudokirchneriella subcapitata* and the marine bacterium *Vibrio fischeri*. Multigenerational toxicity was assessed by measuring the growth inhibition of *P. subcapitata* and acute toxicity was evaluated by measuring the decrease in the constitute bioluminescence of *V. fischeri*. Toxicity study revealed that, degradation of propranolol in ultrapure water showed toxicity in the early stage of irradiation treatment due to accumulation of transformation products but in case of propranolol spiked wastewater toxicity was not observed due to lower rate of oxidation.

Chen et al. (2011) investigated the photodegradation of propranolol by Fe(III)–citrate complexes and effect of metal ions (Ca^{2+}, Mg^{2+}, Mn^{2+} and Cu^{2+}) and humic substances on the photoreactivity of Fe(III)–citrate complexes. Fe(III)–citrate complexes are excellent photocatalysts by generation of hydroxyl radicals, which are main reactive oxygen species responsible for the photodegradation of propranolol. Metal ions inhibited the photodegradation of propranolol by competitive complexation with Fe(III) for citrate and the inhibition effect was in the order of $Mn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$. The presence of humic substances also suppressed the photodegradation of propranolol by competitive complexation of humic substances with citrate for Fe(III). The photolysis experiments were performed in Pyrex vessel under 150-W Xenon Short Arc Lamp and the degradation products formed were identified by GC–MS. 4-hydroxypropranolol, naphthalen-1-ol, 1,5-dihydroxy-naphthalene, 1,6-dihydroxy-naphthalene, some benzene series compounds, and low-molecular-weight carboxylic acids were formed upon photodegradation of propranolol in Fe(III)–citrate system. The proposed pathways for the Fe(III)–citrate-induced photodegradation of propranolol are shown in Fig. 5 (Chen et al., 2011).

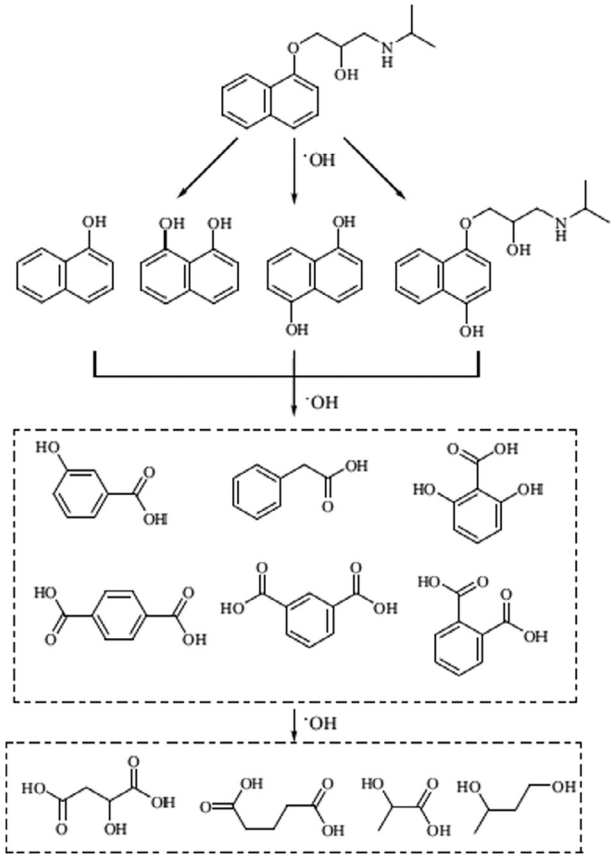


Figure 5 The proposed pathways for the Fe(III)-citrate-induced photodegradation of propranolol (Chen et al., 2011).

Table 1 Summary of the works published on the photocatalysis of β-blockers.

β-Blocker	Matrix	Initial concentration	Catalyst	Irradiation source	Analytical Methods	% removal	References
Metoprolol	Distilled water	0.05 mM	Degussa P25 (1.0 mg/mL), TiO_2 Wackherr (1.0 mg/mL)	UV	HPLC, TOC, HPLC/MS–MS	Complete in 30 min for TiO_2 Wackherr and 60 min for Degussa P25	Abramovic et al. (2011)
Propranolol	Deionized water	0.00002 M	Fe(III)–citrate complex	150 W xenon short arc lamp	HPLC, GC–MS	50 in 37 min	Chen et al. (2011)
Metoprolol	Water	50 mg/dm^3	T1, T2, T3 and T4	UV lamp (254 nm, 0.7 Kw)	UV–Vis spectroscopy COD	50 in 120, 145, 210 and 113 min for T1,T2, T3 and T4, respectively	Czech and Rubinowska (2013)
Propranolol	Milli-Q water	50 mg/L	Degussa P25 (0.4 g/L)	1 Kw Xe-OP lamp, Sun light	HPLC, TOC, BOD_5, COD, Toxicity bioassay by *Chlorella vulgaris*	81 for sun light and 94 for Xe-lamp in 240 min	De la cruz et al. (2013)
Metoprolol	Water	0.05 mM	Mesoporous TiO_2 nanopowder (1 mg/cm^3)	UV	HPLC	Complete in 60 min	Golubovic et al. (2013)
Atenolol propranolol	Pure water and treated municipal water	5–30 mg/L	Degussa P25 (50–3000 mg/L)	1 Kw Xe-OP lamp	Spectrophotometer, TOC, Toxicity bioassay by *D. magna*	80 in 120 min	Ioannou et al. (2011)
Atenolol	pH 6.8 Milli-Q water and river water	37.6 μM	Degussa P25 (2.0 g/L)	High pressure mercury lamp (E_{max} = 365 nm)	HPLC, TOC, HPLC/MS–MS	Complete in 60 and 180 min in pH 6.8 Milli-Q water and river water, respectively	Ji et al. (2013)
Atenolol	Milli-Q water	40 μM	Sodium nitrate (5 mM)	1000 W Xe arc lamp	HPLC, TOC, HPLC/MS–MS, Toxicity bioassay by *D. magna*	72 in 240 min	Ji et al. (2012)
Metoprolol	Aqueous solution	50 mg/L	Titania – coated magnetic activated carbon	1500 W xenon arc lamp (λ > 300 nm, 550 W/m^2)	HPLC, TOC	Complete in 3 h	Rey et al. (2012)
Metoprolol	Aqueous solution	0.0001 M	Degussa P25	Low pressure mercury lamp (E_{max} = 254 nm)	HPLC, TOC	30 for UV-C/1 g/L TiO_2 system and 45 for UV-C/ 0.001 M H_2O_2/ TiO_2 (0.25–2.0 g/L) system in 180 min	Rivas et al. (2010)
Metoprolol propranolol	Milli-Q water	50 mg/L	Degussa P25 (0.4 g/L)	1 Kw Xe-OP lamp	HPLC, TOC, BOD_5, COD, Toxicity bioassay by *Vibrio fischeri*	Complete in 300 min for metoprolol and 360 min for propranolol	Romero et al. (2011)
Propranolol	Ultrapure water, biologically treated wastewater	25 mg/L	Ce-doped TiO_2 (cerium loading of 0.5 wt.% and bulk catalyst concentration of 0.14 g/L)	1 Kw Xe-OP lamp	HPLC, TOC, COD, Toxicity bioassay by *P. subcapitata* and *Vibrio fischeri*	Complete in 90 min in pure water and 360 min in wastewater	Santiago-Morales et al. (2013)
Atenolol Metoprolol Propranolol	Milli-Q water	100 μM	Degussa P25 (2.0 g/L)	High pressure mercury lamp (E_{max} = 365 nm)	HPLC, TOC, HPLC/MS–MS	Complete in 40 min	Yang et al. (2010)

Abbreviations:
HPLC-MS/MS: High performance liquid chromatography-tandem mass spectrometry.
TOC: Total organic carbon.
BOD_5: Biochemical oxygen demand.
COD: Chemical oxygen demand.

Golubović et al. (2013) investigated the efficiency of sol–gel synthesized mesoporous TiO_2 nanopowders for photocatalytic degradation of metoprolol. Mesoporous TiO_2 nanopowders have been synthesized by using titanium tetrachloride ($TiCl_4$) as the precursor. The photocatalytic efficiency of the mesoporous TiO_2 was compared with Degussa P25 and effect of calcination time (1–7 h) on photocatalytic activity of mesoporous TiO_2 was investigated. The mesoporous TiO_2 samples calcined for 4 h have displayed higher photocatalytic performance compared with other calcination time samples due to greater mean pore diameter and the pore structure complexity. Samples calcined for 4 and 5 h have displayed higher photocatalytic performance compared with Degussa P25, whereas the sample calcined for 3 h has shown similar activity. This study indicated that, photocatalytic degradation of metoprolol was strongly effected by pore size and morphology of TiO_2 nanopowders.

An overview of the works published on the photocatalysis of β-blockers is presented in Table 1.

3. Summary

In recent years, the presence of β-blockers in environmental matrices has received a special attention by the scientific community due to increasing use and limited human metabolism (Alder et al., 2010; Huggett et al., 2003; Rivas et al., 2010). After being used, they are released into sewage waste water treatment system and surface waters as metabolites as well as unchanged parent molecules. These compounds are persistent and resistant to biodegradation, accumulating in the environment. They are producing harmful effects (changes in cardiac rhythm, generation of abnormalities, inhibition of the growth of human embryonic cells or reduce mobility of spermatozoids of fish) to aquatic and terrestrial ecosystems (Cleuvers, 2005; Pomati et al., 2006).

Conventional waste water treatments such as activated sludge, granular activated carbon filtration and ozonation were not effective in the removal of these compounds (Maurer et al., 2007; Paxeus, 2004; Vieno et al., 2007) requiring the development of new efficient methodologies. Several studies have reported that AOPs appear as good alternative for the degradation of β-blockers (Andreozzi et al., 2004; Medana et al., 2008; Song et al., 2008; Ternes et al., 2002).

Photocatalysis is an example of AOPs capable of achieving complete oxidation of organic and inorganic species (Calza et al., 2006; Doll and Frimmel, 2005). The catalyst employed for almost all the photocatalytic treatment studies of β-blockers is Degussa P25. It contains 80:20 anatase:rutile shows exceptional activity. Photocatalytic performance of mesoporous TiO_2 nanopowders was high due to greater surface area and optimal exposure of organic molecules to light via facilitation of diffusion of organic molecules to the active sites (Tan et al., 2011; Yu et al., 2007). Doping of TiO_2 with cerium increases the photocatalytic efficiency due to shifting of its absorption from near UV region to the visible region and facile formation of labile oxygen vacancies. Stability of the TiO_2 was increased by preparing TiO_2 magnetic activated carbon catalyst, which is reusable. TiO_2 photocatalysis with ozonation is a promising technology for degradation of drugs in the aquatic environment. In this combined process larger number of hydroxyl radicals was produced compared with single ozonation or TiO_2 photocatalysis. Finally photocatalysis is an efficient and inexpensive treatment technique for the removal of β-blockers from the aquatic environment.

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